Journal of Electroanalytical Chemistry 821 (2018) 73–81

Contents lists available at ScienceDirect

Journal of Electroanalytical Chemistry

journal homepage: www.elsevier.com/locate/jelechem

Poly(gallic acid)/MWNT-modified electrode for the selective and sensitive voltammetric determination of quercetin in medicinal herbs

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ARTICLE INFO

Keywords:
Voltammetry
Modified electrodes
Electropolymerization
Carbon nanotubes
Quercetin
Phytochemical analysis

ABSTRACT

Glassy carbon electrode modified with multi-walled carbon nanotubes and electropolymerized gallic acid (poly (gallic acid)/MWNT/GCE) has been developed for the direct quercetin quantification. The potentiodynamic electropolymerization procedure has been optimized. The best quercetin response has been registered on the polymeric film obtained using 15 cycles from 10 μM gallic acid in phosphate buffer (PB) pH 6.0 in the potential range from − 0.2 to 1.0 V and the scan rate of 100 mV s^{-1}. Scanning electron microscopy (SEM), cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) has been applied for the electrode characterization. The polymeric film has porous structure providing high surface area in comparison to GCE (26.1 ± 4.1 vs. 3.14 mm^2, respectively) as well as gives 1.7-fold decrease of the charge transfer resistance. The poly(gallic acid)/MWNT/GCE response is linear in the ranges of 0.075–25 μM and 25–100 μM of quercetin with the detection limit of 54 nM. The electrode selectivity in the presence of structurally related phenolic compounds is found. The method developed has been successfully applied for the medicinal herbs extract analysis. A good agreement with the independent determination has been obtained.

1. Introduction

Quercetin (3,5,7,3′,4′-pentahydroxyflavone) is one of the important natural phenolic constituents of plants (fruits, vegetables and medicinal herbs) possessing a wide spectrum of bioactivity like antibacterial, anti-inflammatory, anti-allergic and antioxidant properties [1]. The last ones are based on its ability to scavenge free radicals (reactive oxygen and nitrogen species) preventing oxidative damage in living cells [2] and acting as anticarcinogenic [3,4] and antimutagenic [5,6] agent. Therefore, quercetin is substance of interest widely used in medicine (as a major constituent of pharmaceutical dosage forms) and in phytotherapy (as one of the active principals in medicinal herbs). However, the health effects of quercetin are dose-dependent [2,7] and its concentration in sample has to be monitored. On the other hand, quercetin concentration can be considered as parameter for the control of medicinal herbs quality. Therefore, the development of sensitive and selective methods for quercetin quantification is of interest.

As quercetin bioactivity is caused by its participation in electron transfer reaction, the electrochemical methods can be successfully applied for its determination as well as for the investigation of mechanisms of quercetin electrooxidation [8–10] and reactions with radical species. Relatively low sensitivity and lack of the selectivity of traditional stationary electrodes towards target analyte in the case of complex matrix is one of the most important limitations of electroanalysis. But active development of chemically modified electrodes during last decades significantly improved these parameters and enlarged the application fields of electrochemical methods [11].

A wide range of modified electrodes have been developed recently for the quercetin determination. Most of the are based on layer-by-layer modification using carbon nanomaterials (MWNT [12,13], graphene [14]), different types of nanoparticles (flowerlike Co_3O_4 [15], $MnWO_4$ nanocapsules [16]) and composite and hybrid nanomaterials based on combination of carbon nanomaterials, nanoparticles, self-assembled nanolayers (Ag nanoparticles self-assembled onto the surfaces of 2-aminoethanethiol functionalized graphene oxide sheets [17], hexadecyltrimethylammonium bromide/iron decorated MWNT composite [18], cetyltrimethylammonium bromide-carboxylated MWNT [19], mercapto-β-cyclodextrin self-assembled on the Au nanoparticles and MWNT [20], 1-methyl-3-butylimidazolium bromide-NiO-carbon nanotubes nanocomposite [21], Au nanoparticles decorated on porous aromatic framework [22], graphene oxide functionalized with Ag@SiO_2-polyethyleneglycol hybrid core-shell nanoparticles on the Au-printed circuit board [23]). Another type of electrodes used for quercetin determination is based on the polymeric films as sensitive layer (Table 1) including its combination with carbon nanomaterials or metal nanoparticles. Polymeric coverage can be formed using electrolysis

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https://doi.org/10.1016/j.jelechem.2017.12.071
Received 26 October 2017; Received in revised form 25 December 2017; Accepted 29 December 2017
Available online 03 January 2018
1572-6657/